Article

Not peer-reviewed version

# Fully Aromatic Thermotropic Copolyesters Based on Vanillic, Hydroxybenzoic and Hydroxybiphenylcarboxylic Acids

Pavel A. Mikhaylov * , Kirill V. Zuev * , Yaroslav V. Golubev , Valery G. Kulichikhin

Posted Date: 14 May 2024

doi: 10.20944/preprints202405.0927.v1

Keywords: aromatic polyester; thermotropic liquid crystal polymer; TLCP; polycondensation; polymer analysis; DSC; TGA; bio-monomer; vanillic acid

*Article*

# Fully Aromatic Thermotropic Copolyesters Based on Vanillic, Hydroxybenzoic and Hydroxybiphenylcarboxylic Acids

**Pavel A. Mikhailov *, Kirill V. Zuev *, Yaroslav V. Golubev and Valery G. Kulichikhin**

A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences (TIPS RAS), 29 Leninsky Prospekt, 119991 Moscow, Russia; ya_golubev@ips.ac.ru (Y.V.G.); klch@ips.ac.ru (V.G.K.)

* Correspondence: pmih@ips.ac.ru (P.A.M.); zuev.kirill@inbox.ru (K.V.Z.)

**Abstract:** Several series of new polymers were synthesized: binary copolyesters of vanillic (VA) and hydroxybiphenylcarboxylic (HBCA) acids, as well as ternary copolyesters additionally containing hydroxybenzoic acid (HBA) and obtained via three different ways (in solution, in melt and in solid state). The high values of logarithmic intrinsic viscosities and insolubility of several samples proved its high molecular weights. It has been shown that the use of vanillic acid leads to the production of copolyesters with a relatively high glass transition temperature (about 130°C). Thermogravimetric analysis revealed onset of weight loss temperatures of ternary copolyesters occurred at 330-350 °C, the temperature of 5% mass loss is in the range of 390-410 °C. Two-stage thermal destruction is observed for all aromatic copolyester of vanillic acid: decomposition begins with VA units at 420-480 °C, and then decomposition of more heat-resistant units demonstrated above 520 °C. The copolyesters are thermotropic and exhibit a typical nematic type of liquid crystalline order. Mechanical characteristics of copolyesters are close to those for semi-aromatic copolyesters, but are much lower than typical values for fully aromatic thermotropic polymers. Thus, vanillic acid is a mesogenic monomer suitable for the synthesis of thermotropic fully aromatic and semi-aromatic copolyester, but resulting processing temperature must not exceed 280°C.

**Keywords:** aromatic polyester; thermotropic liquid crystal polymer; TLCP; polycondensation; polymer analysis; DSC; TGA; bio-monomer; vanillic acid

---

## 1. Introduction

Thermotropic main-chain polyesters (TMCPs) belongs to a class of high-performance polymer with a number of unique properties [1–9]. TMCP backbone contains aromatic rigid units such as 1,4-phenylene, 2,6-naphthalene and 4,4′-biphenylene, defining the formation of highly ordered nematic melts. This high orientation of macromolecules in the melt allow to produce high tensile modulus and tensile strength fibers and molded articles. Coextrusion of TMCPs and conventional thermoplastics results in self-reinforced composites or composites in situ [9–14]. The mechanical properties of TMCP fibers are comparable to that of aramid fibers [6]. It should be noted, water absorption and atmosphere stability of TMCPs are significantly higher than that of aramid fibers. Typically, TMCPs possess high chemical and heat resistance accompanied with good thermal stability and low thermal expansion coefficient. Thus, TMCPs are used in aerospace field, electronic or optoelectronic devices. High thermal and heat resistance of TMCPs let to produce ovenware from them [15].

Generally, TMCPs represent copolyesters consisting of several monomeric units, because the homopolymers composed from rigid units such as 4-hydroxybenzoate do not melts without decomposition [3,16]. Usually, TMCPs backbone contains rigid mesogenic aromatic para-substituted units with bond angle 180 °C, aromatic units with bond angle differed from 180 °C such as 1,3-phenylene so-called “kinked units”, aromatic units with bulky substituent such as phenyl terephthalic acid and chlorine hydroquinone, and flexible aliphatic spacer such as ethylene glycol. Copolymerization of two of more monomers, introducing "kinked" units and/or aliphatic spacer allow reduce melting point and obtain melt-processable products [1,8]. TMCPs consisting from aromatic units without aliphatic flexible fragments in main-chain are known as thermotropic fully aromatic copolyesters possessing exceptional chemical thermal stability (up to 500 °C in inert atmosphere) unlike the TMCPs with aliphatic flexible spacer which are known as aliphatic-aromatic or semi-aromatic TMCPs.

Basically, fully aromatic TMCPs are produced from conventional oil-based monomers: hydroquinone, 4,4′-dihydroxybiphenol, 4-hydroxybenzoic, 6-hydroxy-2-naphthoic, terephthalic, isophthalic, 2,6-naphtalenedicarboxylic acids and so on. Aliphatic-aromatic TMCPs are prepared by chemical modification of poly(ethylene terephthalate) by 4-acetoxybenzoic acid via ester-ester exchange (X7G Eastman Kodak, Rodrun Unitika) resulting in copolymer of 4-hydroxybenzoic acid with flexible spacer units of PET [17].

The great interest both in academic and industrial fields of the past decades was the use of monomers from biobased renewable sources. The most promising biobased polyester monomers are 2,5-furandicarboxilic, vanillic, syringic, 4-hydroxybenzoic, floretic (3-(4-hydroxyphenyl)propionic), 4-hydroxycinnamic, ferulic (3-methoxy-4-hydroxycinnamic), dihydroferulic acids [18–26]. Structurally, vanillic acid is similar by structure to 4-hydroxybenzoic acid, excluding presence of side -$OCH_3$ group, possessing mesogenic properties, and suitable as comonomer for TMCPs syntheses. The most of recent papers focused on investigation of semi-aromatic TMCPs based on vanillic acid.

Besides the reduced thermal stability, there are several disadvantages of aliphatic-aromatic TMCPs. Aliphatic and aromatic monomers possess poor condensability resulting in low molecular weight and very long polycondensation time [27–30]. A low thermal stability of aliphatic monomer does not allow using high polycondensation temperature.

In the early work H. R. Kricheldorf investigated vanillic acid (VA) homopolymer [31,32]. Some binary VA copolyesters and polyester amides were also described [32–34]. Polyvanillate was intractable polymer, however some binary copolymers were melt processable. Wilsens described [35] a possibility of using vanillic acid as comonomer for fully aromatic copolyester consisting of 4-hydroxybenzoic, 2,5-furandicarboxylic acid, hydroquinone and 4,4′-diphenyldiol. However, Wilsens and coworkers did not obtain high molecular weight of fully aromatic copolyesters of vanillic acid and did not carry out the mechanical properties because they used thin-film polymerization of small amounts of monomers between glass slides.

In the present work, we have synthesized and studied a series of binary copolyesters of vanillic and 4′-hydroxybiphenyl-4-carboxylic acid (HBCA). According to our previous works, HBCA is a promising comonomer for TMCPs [17,36]. Unfortunately, the binary copolyesters did not demonstrate melting or softening at reasonable temperatures. Thus, a series of ternary copolyesters of vanillic, 4′-hydroxybiphenyl-4-carboxylic, and 4-hydroxybenzoic acids were obtained and studied. Some of the ternary copolyesters demonstrated the melting or softening at about 300 °C. The melt-processable ones were converted into thin films by molding and mechanically tested.

## 2. Materials and Methods

### *2.1. Materials*

4-Hydroxybenzoic acid (4HBA, > 99 % purity) was produced by Acros Organics (India). 3-Hydroxybenzoic acid (3HBA, >98% purity) was produced by Reachem (Russia). DMSO-$d_6$ and chloroform-*d* (>99.8 % purity) were purchased from Cambridge Isotope Laboratories (USA). Trifluoroacetic acid (TFA, >98% purity) was offered by Fluka (Switzerland). All other reagents (analytical grade) were purchased from Ekos-1 LLC (Russia).

4-Acetoxybenzoic acid (4ABA) and 3-acetoxybenzoic acid (3ABA) was prepared by refluxing (2 h) corresponding acids in toluene with 20 % molar excess of acetic anhydride according to [31], and then recrystallized from water. 4ABA: $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$, ppm: 8.18–8.12 (m, 2H), 7.26–7.18 (m, 2H), 2.34 (s, 3H). 3ABA: $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$, ppm: 11.68 (s, 1H), 8.00 (d, $J$ = 7.8 Hz, 1H), 7.84 (d, $J$ = 2.4 Hz, 1H), 7.50 (t, $J$ = 7.9 Hz, 1H), 7.36 (dd, $J$ = 8.0, 2.5 Hz, 1H), 2.34 (s, 3H).

4′-Acetoxybiphenyl-4-carboxylic acid (ABCA) was provided by Yaroslavl State Technical University (Russia). $^1$H NMR (400 MHz, $CDCl_3$) δ, ppm: 8.30 (t, *J* = 1.8 Hz, 1H), 8.10 (dt, *J* = 7.9, 1.4 Hz, 1H), 7.86 (dt, *J* = 8.0, 1.4 Hz, 1H), 7.68–7.62 (m, 2H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.23–7.17 (m, 2H), 2.45 (s, 3H).

Food vanillin was used for synthesis of *o*-acetyl vanillic acid after triple extraction with chloroform from aqueous solution using separation funnel. The organic layer was dried over anhydrous $Na_2SO_4$ and chloroform was evaporated under reduced pressure (melting point 84-85 °C).

Vanillic acid (VA) was prepared by caustic fusion of vanillin as previously described [37]. Briefly, KOH (150 g) and water (20 ml) were placed in a 2L stainless steel vessel equipped with overhead wire stirrer and heated to about 120 °C until viscous solution was obtained. Vanillin (60 g) was added portion-wise into the vessel and the temperature was risen to 170 °C for 30 min. The reaction mixture was cooled, recrystallized from water, and dried. Yield of VA: 80 %, melting point 207-210 °C.

*O*-acetyl vanillic acid (AVA) was prepared as previously described [32]. Briefly, vanillin (21 g), acetic anhydride (20 ml), toluene (100 ml), and pyridine (1.25 ml) were refluxed for 3 h. The mixture was concentrated in vacuum, diluted with toluene and concentrated again to remove acetic acid. A brownish residue was dissolved in toluene, recrystallized by portion-wise addition of petroleum ether. Additionally, it was recrystallized twice from chloroform by portion-wise addition of petroleum ether. As a result, colored impurities were removed. Yield of AVA: 60 %, melting point 141-145 °C. $^1$H NMR (400 MHz, chloroform-*d*) δ, ppm: 7.76 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.71 (d, *J* = 1.8 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 1H), 3.91 (s, 3H), 2.34 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ, ppm: 171.28, 168.63, 151.30, 144.52, 128.03, 123.59, 123.11, 113.96, 56.23, 20.79.

## *2.2. Polymer Synthesis*

### 2.2.1. Solution Polycondensation

Binary copolyesters of VA and HBCA (VA-HBCA-1/2, VA/HBCA-1/1, and VA/HBCA-2/1) were prepared by high-temperature solution polymerization in inert solvent Thermolan-H (NPK Polyester LLC, Russia), representing a mixture of hydrocarbons (bp >330 °C) as previously described [32]. Briefly, polycondensation 10 mmol of a mixture AVA and ABCA was carried out in 100 ml three-neck round-bottomed flask equipped with overhead stirrer, argon inlet and short column. The mixture of monomers was immersed in the flask and 50 ml Thermolan (0.2 M concentration of monomers) were added. The argon bubbled through the reaction mixture for 15 min and then the flask was placed to metal bath preheated up to 300 °C. The flask was left in the metal bath for 16 h at 300 °C under continuous flow of argon. Then the flask was cooled under inert atmosphere and the product was collected on a filter and washed with hot acetone in a Soxhlet extractor for at least 8 h. Products are listed in Table 1.

**Table 1.** Comonomer ratio, glass point ($T$g), melting point ($T$m), temperature of onset weight loss ($T$on), temperature of 5 %-weight loss ($T_{5\%}$) of binary copolyesters based on VA and HBCA.

| **Copolyester** | **Molar ratio (AVA / ABCA)** | $T_g$, °C | $T_m$, °C | $T_{on}$, °C | $T_{5\%}$, °C |
|---|---|---|---|---|---|
| B 1/2 | 1:2 | 135.5 | - | 389 | 457 |
| B 1/1 | 1:1 | 135.6 | - | 388 | 424 |
| B 2/1 | 2:1 | 132.5 | - | 382 | 410 |

### 2.2.2. Small-Scale Melt Polycondensation

A small amount of comonomer (VA, 3/4ABA, HBCA) mixture (about 1 g) with different molar ratio were polymerized in 50 ml two-neck round-bottomed flask connected with argon-vacuum line. The flask was filled with argon heated to 240 °C than gradually heated to 320 °C until copolymer was obtained. Products are listed in Table 2.

**Table 2.** Comonomer ratio, glass point ($T$g), melting point ($T$m), temperature of onset weight loss ($T$on), temperature of 5 %-weight loss ($T_{5\%}$) of ternary copolyesters prepared by small-scale melt polycondensation of AVA, ABA and ABCA.

| Copolyester | Molar ratio (AVA / ABA / ABCA) | $T_g$, °C | $T_m$, °C | $T_{on}$, °C | $T_{5\%}$, °C |
|---|---|---|---|---|---|
| T 1/1/1 | 1:1:1 | 117.5 | - | 332.7 | 405.9 |
| T 2/2/1 | 2:2:1 | 116.4 | - | 304.4 | 389.2 |
| T 37/37/26 | 37:37:26 | 116.8 | - | 313.8 | 388.9 |
| T 68/21/21 [1] | *68:21:11* | - | - | - | - |

[1] 3-acetoxybenzoic acid was used instead of 4-acetoxybenzoic acid.

### 2.2.3. Melt Polycondensation

The melt polycondensation in 10-25 g scale was performed in the following procedure. A mixture of AVA, 4ABA, and HBCA was loaded into 100 ml 3-neck round bottomed flask equipped with overhead mechanical stirrer, inert gas inlet, and vacuum outlet. The flask was evacuated and filled with nitrogen three times, then immersed into metal bath preheated to 240 °C under slow flow of argon. After 60 minutes of stirring the temperature was risen every 30 min for 10 °C to 280 °C. After 30 min of stirring at 280 °C the temperature was increased up to 300 °C and after 30 min–up to 320 °C. After the 60 minutes of stirring at 320 °C the vacuum (<1 Torr) was applied for 30 min. The reaction mixture became too viscous for stirring and it was removed from the flask under argon on polyimide film. The product washed with hot acetone in a Soxhlet extractor for at least 8 h. Products are listed in Table 3.

**Table 3.** Comonomer ratio, glass point ($T$g), melting point ($T$m), temperature of onset weight loss ($T$on), temperature of 5 %-weight loss ($T_{5\%}$) of ternary copolyesters prepared by melt polycondensation of AVA, ABA and ABCA.

| Copolyester | Molar ratio (AVA / ABA / ABCA) | $T_g$, °C | $T_m$, °C | $T_{on}$, °C | $T_{5\%}$, °C |
|---|---|---|---|---|---|
| TM 1/1/1 | 1:1:1 | 120.8 | - | 339.1 | 408.7 |
| TM 1/2/1 | 1:2:1 | 117.0 | - | 310.5 | 399.7 |

### 2.2.4. Melt Polycondensation Accompanied with Solid-State Polycondensation

The polycondensation in 10-25 g scale was performed according to the following procedure. A mixture of AVA, 4ABA, and HBCA was loaded into 100 ml 3-neck round bottomed flask equipped with overhead mechanical stirrer, inert gas inlet, and vacuum outlet. The flask was evacuated and filled with nitrogen three times, then immersed into metal bath preheated to 240 °C under slow flow of argon. After 60 minutes of stirring the temperature was risen every 30 min for 10 °C to 280 °C. After 30 min of stirring at 280 °C prepolymer was removed from the flask on polyimide film. The prepolymer was grounded, placed in a vessel and heated at 250-260°C for 8-16 h under continuous flow of argon or vacuum (< 0.1 Torr). Products are listed in Table 4.

**Table 4.** Comonomer ratio, glass point ($T$g), melting point ($T$m), temperature of onset weight loss ($T$on), temperature of 5 %-weight loss ($T_{5\%}$) of ternary copolyesters based on AVA, ABA and ABCA, prepared by solid-state polycondensation of prepolymers. The SSP conditions are also indicated.

| Copolyester | Molar ratio (AVA / ABA / ABCA) | SSP condition: temperature, °C (time, h) | $[\eta]$ | $T_g$, °C | $T_m$, °C | $T_{on}$, °C | $T_{5\%}$, °C |
|---|---|---|---|---|---|---|---|
| TS 1/1/1-8 | 1:1:1 | 250 (8) | 6.3 | 114.0 | - | 325.1 | 389.8 |
| TS 1/1/1-16 | | 250 (8) + 255 (8) | 8.7 | 116.8 | - | 334.9 | 391.4 |
| TS 37/37/26-8 | 37:37:26 | 250 (8) | 13.8 | 113.1 | - | *n/a* | *n/a* |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| TS 37/37/26-16 | | 250 (8) + 255 (8) | *insol.* | 119.6 | - | 349.7 | 394.9 |
| TS 1/3/1-8 | 1:3:1 | 250-260 (8) | *insol.* | 106.7 | - | *n/a* | *n/a* |
| TS 1/3/1-16 | | 260 (16) | *insol.* | 108.1 | - | 357.3 | 408.2 |

### 2.3. Comonomer and Polymer Characterization

$^1$H NMR spectra of comonomers were recorded on AVANCE III HD spectrometer (Bruker, Germany) with an operating frequency of 400 MHz. DMSO-$d_6$ or CDCl$_3$ were used as solvents.

The measurement of logarithmic viscosity ($[\eta]$) for polymers was carried out at 60 ± 0.1 °C using an Oswald viscometer with 0.6 mm capillary and calculated by equation 1:

$$[\eta] = ln(t/t_0)/c, \tag{1}$$

where: $t$, $t_0$–time of flow the polymer solution and time of flow pure solvent though capillary, respectively; $c$—concentration of polymer solution, 0.1 g of polymer in 100 g pentafluorophenol.

FTIR spectra were recorded in the reflection mode on a Hyperion-2000 IR-microscope coupled to an IFS-66 v/s IR-Fourier spectrometer (Bruker, Billerica, MA, USA): crystal Ge, resolution 2 cm$^{-1}$, wavelength range 4000–600 cm$^{-1}$.

X-ray diffraction analysis (XRD) was performed using a rotating copper anode Rotaflex RU-200 (Rigaku, Japan) in 50 kV–100 mA source operating mode. The X-ray source was equipped with a horizontal wide-angle D/Max-RC goniometer and a secondary graphite monochromator (emission wavelength $\lambda$ = 1.542 Å). The range of diffraction angles was 5–60 ° in 2$\theta$, and measurements were carried out in the continuous scanning mode at a rate of 2 °/min (step 0.04°). $\theta$–2$\theta$ scanning was performed according to the Bragg–Brentano scheme.

DSC/TGA analysis of binary copolyesters was performed on TGA/DSC3+ thermal analysis instrument (Mettler Toledo, Columbus, OH, USA) in the temperature range from 30 to 1000 °C at a heating rate of 10 °C/min. The inert gas flow rate (argon) was 100 cm$^3$/min.

DSC thermograms of ternary copolyesters were obtained using DSC 204F1 instrument (Netzsch, Selb, Germany) in the following mode: heating from 20 to 350°C at a rate of 10°C/min, then cooling to 20°C at a rate of 10°C/min, then reheating 10°C/min to 350°C. The analysis was carried out in an inert atmosphere (argon, flow rate 40 ml/cm$^3$).

TGA analysis of ternary copolyesters was carried out on STA 449F3 Jupiter instrument (Netzsch, Selb, Germany) in the following mode: heating from 25 to 1000°C at a rate of 10°C/min; the analysis was performed in an inert atmosphere (argon, flow rate 50 ml/cm$^3$).

The optical properties of thin layers of copolyester melts were studied using a 6 PO polarizing optical microscope (Biomed, Moscow, Russia) equipped with a FP900 heating table (Mettler, Columbus, OH, USA) and an E3ISPM5000 photo/video camera (ToupTek Photonics Co., Zhejiang, China), in the following mode: heating to 350 °C and cooling to 25 °C (10-20 °C/min).

The mechanical characteristics of ternary polyesters (tensile strength and relative elongation at break) were assessed during tensile testing of film samples (thickness 100 μm) on I1140M-5-01-1 instrument (TOCHPRIBOR-KB, Ivanovo, Russia); a 100 N load cell was used and the loading speed was 10 mm/min; test temperature was 25°C.

## 3. Results and Discussion

### 3.1. Binary Copolyesters

Unsubstituted and substituted derivatives of hydroxybenzoic acids are widely used for syntheses of TMCPs [1,8], however 4-hydroxybenzoic acid itself is not quite suitable as monomer because of the decarboxylation by-process at about 200 °C [16]. So usually, acetoxybenzoic acids prepared by acetylation of hydroxybenzoic acids are used as the monomers. The general route for binary and ternary copolymer syntheses from acetoxy acids is presented in Figure 1.

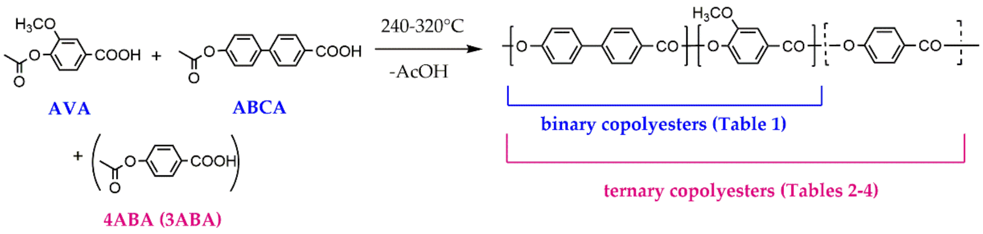


**Figure 1.** Binary and ternary copolyester syntheses route.

There are three possible ways to synthesize polyesters: solution polycondensation (SP), melt polycondensation (MP), and solid-state polycondensation (SSP). High melting point polyesters, including non-meltable, can be synthesized by SP and SSP procedures. Copolyesters which melting or softening points lower than decomposition point can be synthesized by MP method. Thus, binary copolyesters of VA and HBCA (B1/2, B1/1, and B2/1) were synthesized by solution polycondensation from AVA and ABCA at 300 °C (Table 1). Thermolan H was used as high temperature solvent representing a mixture of aromatic hydrocarbons with b.p. > 330 °C.

Characterization of the binary copolymers was carried out by FTIR method (Figure 2) because of its insolubility in common solvent. Very strong band C=O vibration ($\nu_{C=O}$) of ester groups appeared at 1729 $cm^{-1}$ for B1/2, shifted to 1731 $cm^{-1}$ for B1/1, and to 1732 $cm^{-1}$ for B2/1. This shift is entirely consistent with the fact that C=O vibration of ester groups appeared at 1727 $cm^{-1}$ for HBCA homopolymer and 1735 $cm^{-1}$ for polyvanillate [32,38]. Benzene ring stretching vibrations ($\nu_{C=C}$) appeared at about 1600 $cm^{-1}$ and 1500 $cm^{-1}$. Stretching vibration of C-O ($\nu_{C-O}$) bond in VA units appeared at 1283 $cm^{-1}$ and 1028 $cm^{-1}$ and their intensity increases with increasing VA/HBCA ratio in the copolymers. Absorption peaks at 763 $cm^{-1}$, 749 $cm^{-1}$, 713 $cm^{-1}$, and 694 $cm^{-1}$ are related to in-plane bending vibrations of para- and 1,2,4-substituted phenyl rings.

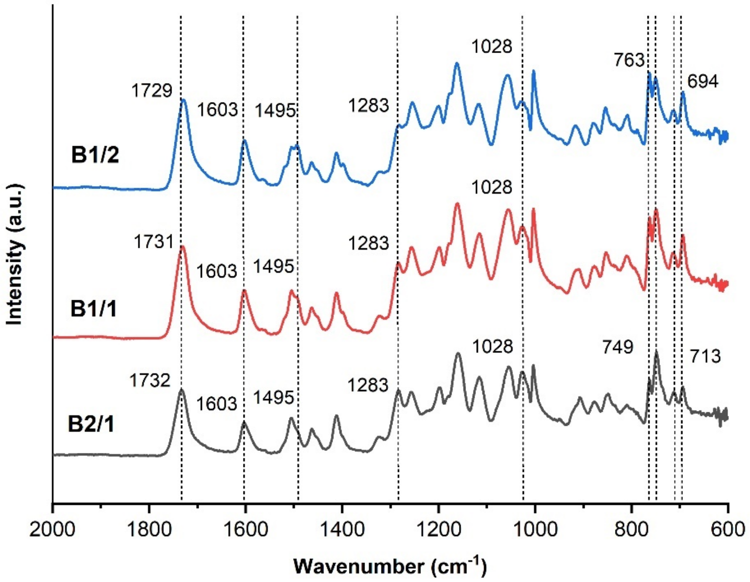


**Figure 2.** FTIR-ATR spectra of binary copolyesters based on VA and HBCA (B2/1, B1/2, and B2/1).

Thermal properties of binary copolyesters were analyzed by DSC-TGA method. The glass transition points are slightly lowered from 135.5 °C to 132.5 °C with increase of VA content in copolyester (Figure 3). The $T_g$ points are higher than that of copolyester Vectra A950 with $T_g$ = 93 °C composed from 2-hydroxy-6-naphtoic and *p*-hydroxybenzoic linear units [39]. These was explained by effect of bulky substituent $–OCH_3$ in VA units decreasing chain mobility, that was observed for other TMCPs [40]. DSC was not shows melting of B1/2-B2/1, i.e., these polymers have very low crystallinity degree.

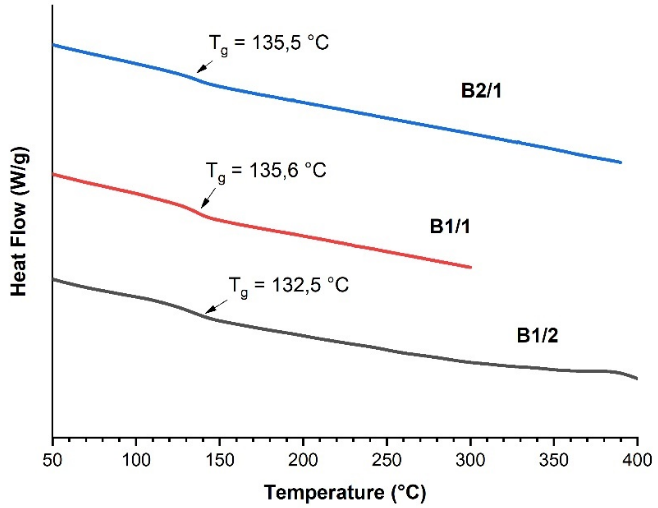
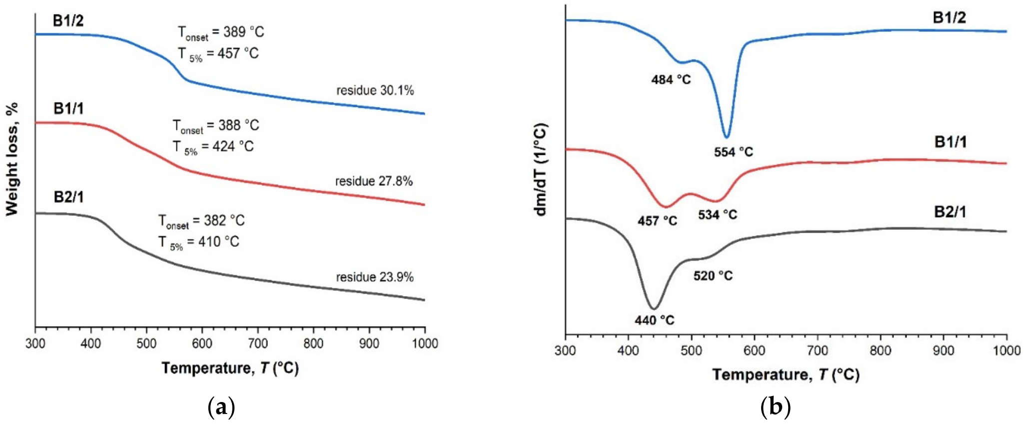


**Figure 3.** DSC thermograms of binary copolyesters based on VA and HBCA (B2/1, B1/2, and B2/1) in the second heating cycle at a rate of 10 °C/min in an inert atmosphere.

TGA thermograms (Figure 4a) demonstrate the decomposition onset temperature ($T_{on}$) and the temperature of 5% weight loss ($T_{5\%}$) were lowered with increase of VA content in the copolyesters. DTG curves (Figure 4b) of the binary copolyesters shows two-stage decomposition process with two minimums: the first one is observed at temperature below 500 °C and the second one—higher than 500 °C. The first minimum belongs to VA units' decomposition and the second one to HBCA decomposition. Thus, increasing molar fraction of VA units results in decreasing thermal stability of copolyesters. Additionally, this is reflected on the amount of mass remaining after decomposition at heating to 1000°C: 30.1% for B1/2 and 23.9% for B2/1. Although B2/1 can be molded with short-time exposition at 350 °C, TGA data indicates that such high temperature for B2/1 rather is not applicable since material darkening is observed.



(**a**) (**b**)

**Figure 4.** TGA (**a**) and DTG (**b**) curves for binary polyesters based on VA and HBCA (B2/1, B1/2, and B2/1) in an inert atmosphere, heating rate of 10 °C/min.

Copolyesters B1/2 and B1/1 are not processable because of high viscosity while B2/1 was molded at 350 °C in order to visualize the formation of the liquid crystalline phase. Polarized optical microscopy (POM) of B2/1 demonstrated mesophase formation (Figure 5), but due to the high melt viscosity, it was difficult to obtain a sufficiently thin layer of the microslide.

doi:10.20944/preprints202405.0927.v1

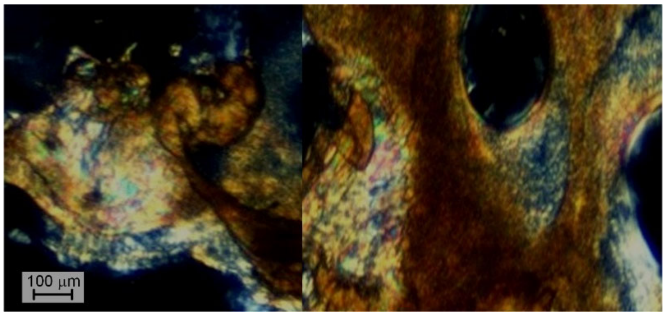


**Figure 5.** Polarized optical microscopy of binary copolyester B2/1 melt at 350°C.

In general, it can be said that the binary copolyesters of VA and HBCA do not have acceptable characteristics: these polymers have a softening point that is too high, close to the beginning of the decomposition of vanillic acid units. At the same time, despite the ability of polyesters to form a mesophase at a high VA content, such melts are unacceptably viscous for effective processing.

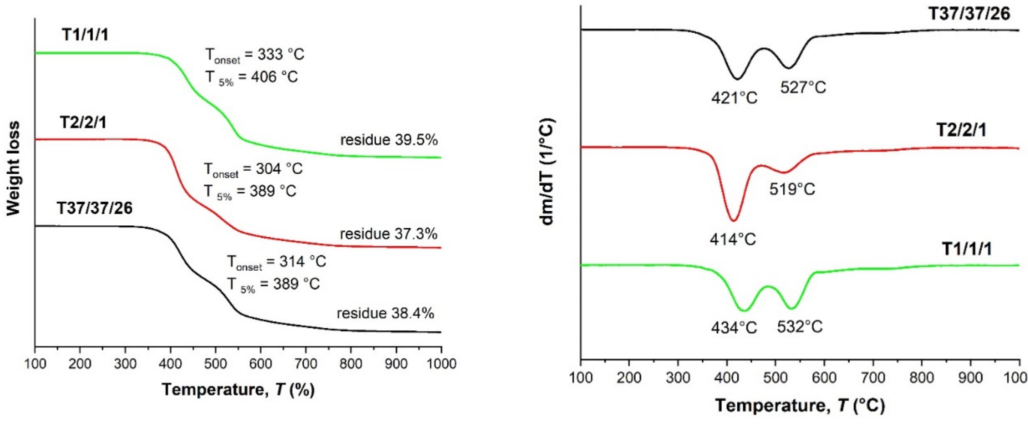
To reduce the softening point, we synthesized ternary copolyesters containing HBA units in addition to VA and HBCA.

### *3.2. Ternary Copolyesters*

Wilsens and coworkers applied thin film polycondensation with small amount of monomers to study composition of potential melt processable copolyester [35,41]. In present study as well as in our previous work [42] we applied small-scale (about 1 g of monomers) polycondensation in the flask in inert atmosphere in 240-320 °C range. These allowed more thoroughly visually control the polycondensation process and the viscosity evolution. When the viscosity was increased, the polycondensation was stopped and product was evacuated from the flask. Much attention was paid to composition with reduced molar content of ABCA. The results are presented in Table 2. Additionally, the ternary copolyester T68/21/11 was prepared from AVA, ABCA and 3-acetoxybenzoic acid (3ABA) which is similar to previously described ternary copolyester with composition: HBA (70%), HBCA (20 %) and 3HBA (10%) which was melted at 315 °C [36]. The copolyester T1/1/1, T2/2/1, T37/37/26 were soften at about 300 °C. The preparation of T68/21/21 was failed because after 15 minutes of polycondensation of the monomers at 280°C, the reaction mass solidified and raising the temperature to 320°C had no effect. This was unexpected since the copolyester HBA (70%), HBCA (20%) and 3HBA (10%) was melt processable. Typically, the introduction of side substituents reduces the melting or softening point of the resulting copolyester. Although VA unit structurally is HBA unit with a bulky substituent, the HBA and VA units play different roles in thermal properties.

The ternary copolymers VA-HBA-HBCA are also non-crystalline. At the same time, they have noticeably lower glass transition temperatures (about 117 °C) even compared to binary copolyesters VA-HBCA (about 135 °C), and especially compared to copolyesters 3HBA-3HBCA (4′-hydroxybiphenyl-3-carboxylic), for which $T_g$ can reach 190 °C [42]. As has been repeatedly shown, including in our early works [17,36], in polyesters based on aromatic hydroxy acids, a comonomer with biphenyl units, in this case HBCA, makes a large contribution to heat resistance. The ratio of biphenyl and monophenyl comonomer units in binary copolymers VA-HBCA is higher than in ternary copolymers VA-HBA-HBCA, which leads to a decrease $T_g$ values.

As in the case of binary copolyesters, terpolymers also show a stepwise thermal decomposition pattern (Figure 6) with two weight loss maxima: around 410-430 °C and 520-530 °C. In addition, ternary copolyesters have noticeably lower temperatures for the onset of weight loss (300-330 °C) and 5% weight loss (390-410 °C). This is probably due to a decrease in the HBCA/VA ratio, since in the series T2/2/1, T37/37/26, T1/1/1, an increase in thermal stability can be noted with an increase in the content of biphenyl HBCA units. However, the weight residue after decomposition is higher for ternary copolyesters, that can be explained by presence of a large portion of HBA units, which themselves have high thermal stability.



(**a**) (**b**)

**Figure 6.** TGA (**a**) and DTG (**b**) curves for ternary polyesters based on VA, HBA and HBCA, prepared by small-scale melt polycondensation; analysis performed in an inert atmosphere at heating rate of 10 °C/min.

Next, a series of high-molecular-weight ternary copolyesters were obtained using the melt polycondensation at 240-320 °C. A traditional method was applied, using a 100 ml three-neck round bottom flask equipped with an overhead glass stirrer, argon inlet and vacuum outlet on a scale of 15-25 g. The temperature was gradually increased from 240°C to 320°C. The final stage was carried out at a temperature of 320 °C in vacuum. The polycondensation was stopped when the desired viscosity was reached. The products prepared are listed in Table 3. Polymers TM1/1/1 and TM1/2/1 are not dissolved in pentafluorophenol at 80 °C, only swelling was observed.

During the melt polycondensation darkening of the reaction mixture was observed at temperatures above 280 °C. To avoid the destructive processes, a combined method was used. The first stage was carried out in the melt at a temperature of 240-280 °C in argon atmosphere. Then the prepolymers were crushed and polymerized in the solid state at 250-260 °C in vacuum or argon atmosphere for 8-16 hours (Table 4). Despite the decrease in polycondensation temperature, colored products were still obtained. Copolyester TS1/3/1 with a lower VA content was less colored compared to the others. Thus, the color change was caused by the presence of VA units in the copolyesters. All copolyesters listed in Tables 3 and 4 were relatively ductile and their logarithmic viscosities values were high. Some of the copolyesters were insoluble in pentafluorophenol due to their high molecular weight. In this regard, IR spectroscopy was also used to confirm the structure of copolyesters.

The FTIR spectra of the ternary copolyesters are presented in Figure 7 and contain all the characteristic absorption bands as the spectra of the binary copolymers. The C=O vibration band ($\nu_{C=O}$) of the ester groups is shifted to 1728 cm$^{-1}$. Stretching vibrations of the C-O bond ($\nu_{C-O}$) in VA units appeared at 1283 cm$^{-1}$ and 1028 cm$^{-1}$ in the form of a shoulder due to the decrease in the number of VA units. Benzene ring stretching vibrations ($\nu_{C=C}$) and the bending vibrations are presented in the same region as in binary copolyesters: 1600, 1500, 763, 749, 713 and 694 cm$^{-1}$.

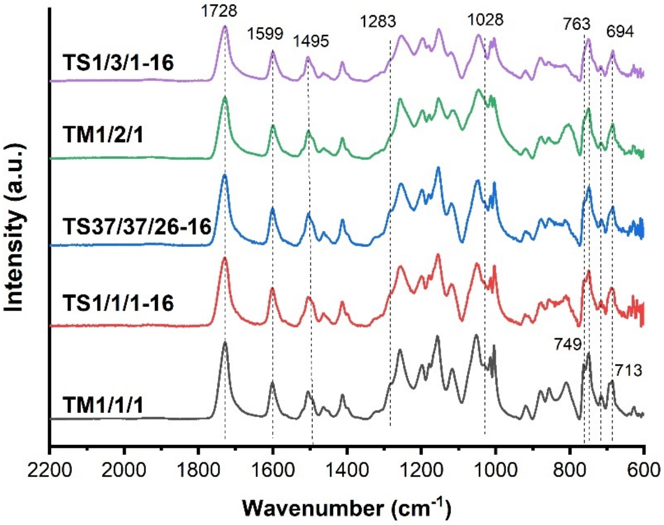


**Figure 7.** FTIR-ATR spectra of ternary copolyesters of VA, HBA and HBCA, prepared by melt polycondensation and solid-state polycondensation.

X-ray diffraction patterns were obtained for a number of ternary polyesters with different comonomer ratios in the 2$\theta$ range from 5 to 60° (Figure 8). All ternary copolyesters do not show sharp reflections of crystalline phases, but only a broad halo with a maximum of about 20°, which indicates their low degree of crystallinity. All three comonomers (VA, HBA, HBCA) are structurally similar and have similar XRD patterns. The peak at 20° is characteristic of both structural fragments of HBCA [17,43] and HBA [44]. At the same time, a sharper peak is usually observed for biphenyl fragments of HBCA, and a broadened one for HBA. Thus with an increase in the HBCA/HBA ratio from TS1/3/1 to TS37/37/26, a narrowing of the reflex at 20° can be noted. According to [32], for structural fragments of vanillic acid peaks are observed in the region of 15-20° and at 25°, but when the ratio of VA with other comonomers is equalized, all peaks disappear. This explains the absence of additional peaks in the XRD patterns for terpolymers, especially considering the low content of VA compared to other comonomers.

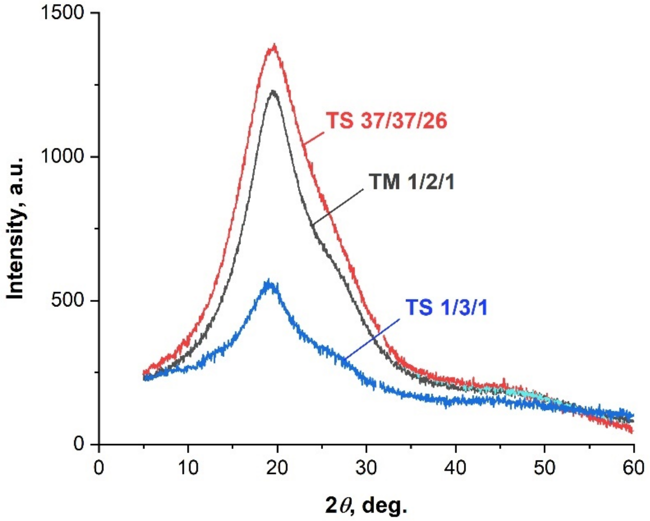
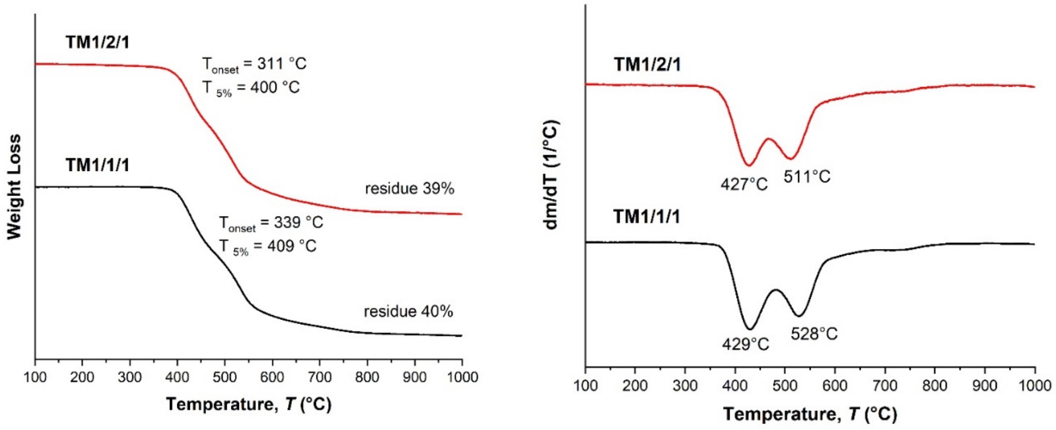


**Figure 8.** XRD patterns of ternary copolyesters of VA, HBA and HBCA.

Terpolymers obtained by melt polycondensation and using a solid-state process demonstrates similar thermal characteristics. They have a relatively low glass transition temperature in the region

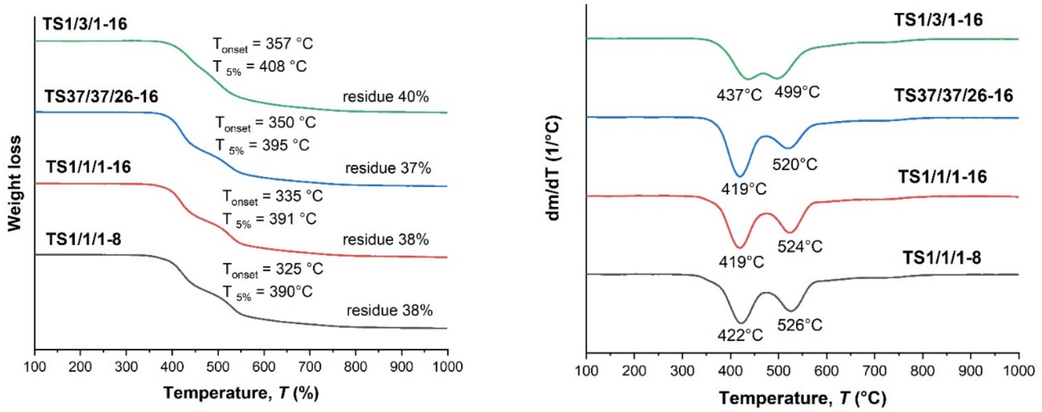
doi:10.20944/preprints202405.0927.v1

of 110-120 °C (Tables 3 and 4) and a stepwise behavior of thermal decomposition (Figures 9 and 10). For all samples, the typical temperature for the onset of mass loss lies in the range of 330-350 °C, the temperature of 5% mass loss is in the range of 390-410 °C, the weight residue at 1000 °C is about 40%.



(**a**) (**b**)

**Figure 9.** TGA (**a**) and DTG (**b**) curves for ternary copolyesters prepared by melt polycondensation of AVA, ABA and ABCA; analysis performed in an inert atmosphere at heating rate of 10 °C/min.



(**a**) (**b**)

**Figure 10.** TGA (**a**) and DTG (**b**) curves for ternary copolyesters based on AVA, ABA and ABCA, prepared by solid-state polycondensation of prepolymers; analysis performed in an inert atmosphere at heating rate of 10 °C/min.

The ternary copolyesters with the same composition, but obtained by different methods (in solution, in the melt, in solid phase) evidently possessing different molecular weights, no significant differences in thermal characteristics were showed. Table 5 shows the results for different VA/HBA/HBCA copolyester samples with a ratio of 1/1/1, so no significant difference was found in the thermal stability of copolyesters subjected to solid-state polycondensation for different times (8 and 16 hours). This fact is not unexpected: for example, in papers [45,46] is shown, that for similar copolyesters in a wide range of molecular weights, the thermal characteristics differ insignificantly.

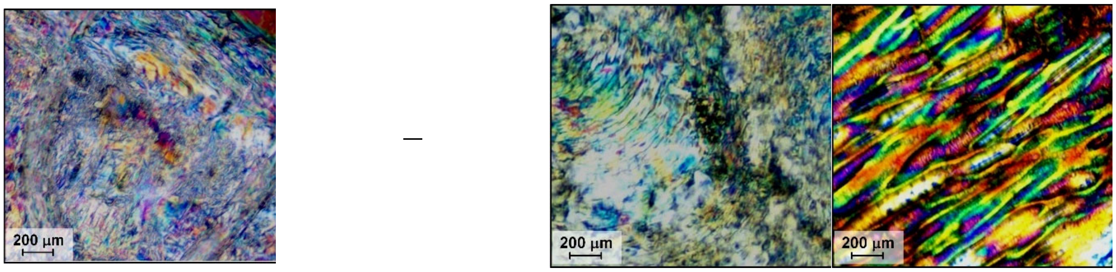
In general, the introduction of VA into macromolecule backbone drastically reduces their thermal stability. TGA showed that the decomposition started at 330 °C, so visual observations at 280 °C. Therefore, VA copolymers preferably should additionally contain aliphatic comonomers to reduce the processing temperature less than 280 °C.

**Table 5.** Comparison of the thermal characteristics of ternary copolyesters VA-HBA-HBCA of the same comonomer composition, obtained by different methods.

| Copolyester | Molar ratio (AVA / ABA / ABCA) | [$\eta$] | $T_g$, °C | $T_{on}$, °C | $T_{5\%}$, °C | *residue at 1000°C* |
|---|---|---|---|---|---|---|
| T 1/1/1 | 1:1:1 | 1.2 | 118 | 333 | 406 | 40 |
| TM 1/1/1 | | *insol.* | 121 | 339 | 409 | 40 |
| TS 1/1/1-8 | | 6.3 | 114 | 325 | 390 | 38 |
| TS 1/1/1-16 | | 8.7 | 117 | 335 | 391 | 38 |

The existence of a liquid crystalline phase of ternary copolyesters VA/HBA/HBCA with various comonomer compositions - 1/1/1, 1/2/1, 1/3/1 (Figure 11) was confirmed by polarization optical microscopy (POM). Generally, TMCPs exhibit a schlieren texture typical for nematic melts. Similar results were obtained for copolyesters based on hydroxy acids, aromatic diols / diacids of various structures [17,41,47,48].

The ternary copolyesters do not demonstrated isotropization up to 375 °C, which is apparatus limit and higher than decomposition temperature. After cooling liquid crystalline (LC) melts saved the texture, thus the formation of LC glasses was observed. As an example, Figure 12 shows micrographs obtained by heating copolyester T1/1/1 from a temperature below the glass transition to the temperature of mesophase formation throughout the entire volume of the melt. It can be noted that when the glass transition temperature is exceeded and as the viscosity of the melt decreases, the formation, growth and coalescence of LC phase droplets occur.



(**a**) (**b**) (**c**) (**d**)

**Figure 11.** Polarized optical microscopy of ternary copolyesters: (**a**) T1/1/1 at 300 °C; (**b**) T37/37/26 at 300 °C; (**c**) TM1/2/1 at 340 °C; (**d**)—TS1/3/1 at 300 °C.

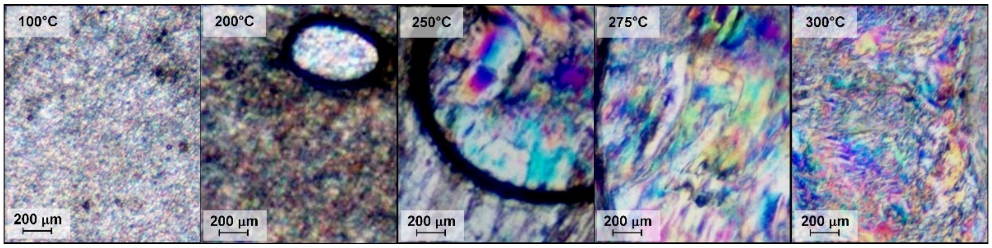


**Figure 12.** Polarized optical microscopy of ternary copolyester T1/1/1 during its heating from 100 to 300 °C with a rate 10°C/min.

The mechanical characteristics of ternary polyesters (tensile strength, relative elongation at break, elasticity modulus) were measured by tensile testing of film samples. The copolyesters thin film (thickness 100 μm) were molded by hot pressing at 300 °C.

Tests were carried out for polyesters: TM1/1/1, TM1/2/1, TS37/37/26 and TS1/3/1. Unfortunately, it was not possible to achieve high strength characteristics for these copolymers. Average values of mechanical characteristics are as follows: tensile strength is 39 MPa, elastic modulus is 125 MPa and relative elongation at break of 4%. These characteristics are close to those for semi-aromatic copolyesters of polyethylene terephthalate and HBCA [17], but are much lower than typical values for fully aromatic thermotropic polymers. We assume that this problem is associated with a fairly high softening temperature of the copolyesters, which lies close to the region of thermal degradation. In this regard, VA should be used for copolyesters with moderate thermal stability and additional comonomers reducing processing point should be included into macromolecular backbone of the copolyesters.

Wilsens and coworkers used VA as comonomers for TMCPs in amount of 10 and 16 molar %. [13,23,49,50]. On the other hand, ternary copolyester of HBA/HNA/VA with 5 % molar content of VA demonstrated lowered melting point, increased glass transition temperature, good thermal stability, and excellent spinnability [51]. In combination with the results obtained in our research, it can be stated that vanillic acid can be used as additive comonomer for TMCPs synthesis with content not exceeding 10-20 mol. % and do not considered as the major comonomer. The higher amount of VA in TMCPs results in decreased thermal stability and increased of melt viscosity due to the presence of bulky –$OCH_3$ hindering chain mobility.

## 4. Conclusions

In this research, we attempted to obtain fully aromatic polyesters using bioavailable vanillic acid as a comonomer. Several series of new polymers were synthesized: binary copolyesters of vanillic (VA) and hydroxybiphenylcarboxylic (HBCA) acids, as well as ternary copolyesters, additionally containing hydroxybenzoic acid (HBA) and obtained in three different ways (in solution, in melt and in solid state).

It has been shown that the use of vanillic acid leads to preparing copolyesters with a relatively high glass transition temperature (about 130°C). At the same time, the heat resistance of binary VA-HBCA copolymers was higher than that of ternary copolymers VA-HBA-HBCA, which was explained by decrease of biphenyl moiety in ternary copolyesters in comparison with than that of binary copolyesters. The onset of weight loss of ternary copolymers occurs at 330-350°C, the temperature of 5% mass loss is in the range of 390-410 °C. At the same time, binary and ternary copolyesters of vanillic acid demonstrated two-stage thermal destruction is observed: decomposition starts with VA units at 420-480°C, and then decomposition of more heat-resistant units occurs above 520°C.

The copolyesters are thermotropic and exhibit a typical nematic type of liquid crystalline state in the melt at temperatures above the glass transition point. Ternary copolymers VA-HBA-HBCA form LC melts more readily due to the lower melting temperature, in contrast to binary copolymers VA-HBCA. The isotropization temperatures were higher than the temperature of thermal destruction.

Mechanical characteristics of the copolyesters are close to those for semi-aromatic copolyesters, but are much lower than for fully aromatic thermotropic polymers. We assume that this problem is associated with a fairly high softening temperature of such copolyesters, which lies close to the region where thermal degradation begins. In this regard, VA should be used for copolyesters with moderate thermal stability and additional comonomers reducing processing point should be included into macromolecular backbone of the copolyesters.

Summarizing the data, vanillic acid can be used as additive comonomer for TMCPs synthesis with content not exceeding 20 mol. % (more preferably not exceeding 10 mol. %) and do not considered as the major comonomer. The higher amount of VA in TMCPs results in decreased thermal stability and increased of melt viscosity.

**Author Contributions:** Conceptualization, V.G.K. and P.A.M.; synthesis and validation of copolyesters, P.A.M.; microscopy, K.V.Z.; thermal analysis, Y.V.G.; writing—original draft preparation, P.A.M. and K.V.Z.; writing—review and editing, V.G.K.; visualization, K.V.Z.; project administration, K.V.Z. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was carried out with the financial support of Russian Science Foundation (RSF, grant number 22-73-00257, https://rscf.ru/project/22-73-00257/) and within the State Program of A.V. Topchiev Institute of Petrochemical Synthesis (TIPS RAS).

**Data Availability Statement:** The data presented in this study are available on request from the corresponding author.

**Acknowledgments:** In this work FTIR-ATR and XRD analyzes were performed using the equipment of the Shared Research Center «Analytical center of deep oil processing and petrochemistry of TIPS RAS». Authors thank Friederich Menges (Oberstdorf, Gemany) for providing a free academic license of the Spectragryph optical spectroscopy software.

**Conflicts of Interest:** The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

## References

1. Jin, J.I.; Kang, C.S. Thermotropic main chain polyesters. *Progress in Polymer Science* **1997**, *22*, 937–973.
2. Jackson, W.J. Liquid Crystal Aromatic Polyesters: Early History and Future Trends. *Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics* **1989**, *169*, 23–49.
3. Economy, J. Aromatic Polyesters of p -Hydroxybenzoic Acid. Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics **1989**, 169.
4. Deberdeev, T.R.; Akhmetshina, A.I.; Karimova, L.K. et al. Heat-Resistant Polymer Materials Based on Liquid Crystal Compounds. *Polym. Sci. Ser. C* **2020**, *62*, 145–164.
5. Lyu, X.; Xiao, A.; Shi, D. et al. Liquid crystalline polymers: Discovery, development, and the future. *Polymer* **2020**, *202*, 122740.
6. Limeneh, D.Y.; Yilma, K.T. Review on Vectran-Super Fiber from Thermotropic Crystals of Rigid-Rod Polymer. *Journal of Engineering* **2021**, 6646148.
7. Roeting, O.; Hinrichsen, G. Blends of thermotropic liquid-crystalline and thermoplastic polymers—a short review. *Advances in Polymer Technology* **1994**, *13*, 57–64.
8. Han, H.S.; Bhowmik, P.K. Wholly aromatic liquid-crystalline polyesters. *Progress in Polymer Science* **1997**, *22*, 1431–1502.
9. Kulichikhin, V.G.; Platé, N.A. Blend composites based on liquid crystal thermoplast. *Polymer Science U.S.S.R.* **1991**, *33*, 1–37.
10. Kim, J.Y.; Kang, S.W.; S.H. Kim. Thermotropic liquid crystal polymer reinforced poly(butylene terephthalate) composites to improve heat distortion temperature and mechanical properties. *Fibers and Polymers* **2006**, *7*, 358–366.
11. Yang, Q.; Hirata, M.; Hsu, Y.-I. et a. Improved Thermal and Mechanical Properties of Poly(butylene succinate) by Polymer Blending with a Thermotropic Liquid Crystalline Polyester. *Journal of Applied Polymer Science* **2014**, *131*, 39952.
12. Choi, J.-K.; Lee, B.-W.; Choi, Y.-S. et al. Reinforcing Properties of Poly(trimethyleneterephthalate) by a Thermotropic Liquid Crystal Polymer. *Journal of Applied Polymer Science* **2015**, *132*, 41408.
13. Wilsens, C.H.R.M.; Pepels, M.P.F.; Spoelstra, A.B. et al. Improving Stiffness, Strength, and Toughness of Poly(ω-pentadecalactone) Fibers through in Situ Reinforcement with a Vanillic Acid-Based Thermotropic Liquid Crystalline Polyester. *Macromolecules* **2016**, *49*, 2228–2237.
14. de Kort, G.W.; Bouvrie, L.H.C.; Rastogi, S. et al. Thermoplastic PLA-LCP Composites: A Route toward Sustainable, Reprocessable, and Recyclable Reinforced Material. *ACS Sustainable Chemistry & Engineering* **2020**, *8*, 624–631.
15. Sirigu, A. Topics in the evolution of liquid crystal polymers. *Liquid Crystals* **1993**, *14*, 15–36.
16. Economy, J.; Storm, R.S.; Matkovich, V.I. et al. Synthesis and structure of para-hydroxybenzoic acid polymer. *Journal of Polymer Science Part A-Polymer Chemistry* **1976**, *14*, 2207–2224.
17. Mikhaylov, P.A.; Zuev, K.V.; Filatova, M.P. et al. Synthesis and Properties of Thermotropic Copolyesters Based on Poly(ethylene terephthalate) and 4′-Acetoxy-4-biphenyl-carboxylic Acid. *Polymers* **2021**, *13*, 1720.
18. Fei, X.; Zhang, X.; Liu, J. et al. Synthesis of a fire-retardant and high Tg biobased polyester from 2,5-furandicarboxylic acid. *Polymer Journal* **2022**, *54(8)*, 1-14.
19. Bazin, A.; Averous, L.; Pollet, E. Lipase-catalyzed synthesis of furan-based aliphatic-aromatic biobased copolyesters: Impact of the solvent. *Eur. Polym. J.* **2021**, *159*, 110717.
20. Singh, M.; Takada, K.; Kaneko, T. Biobased liquid crystalline poly(coumarate)s composites and their potential applications. *Composites Communications* **2020**, *22*, 100531.
21. Wei, P.; Zhang, W.; Zhang, Y. Direct synthesis of potentially biodegradable aromatic-aliphatic thermotropic copolyesters with photocrosslinking properties. *Liquid Crystals* **2019**, *46*, 1780–1789.
22. Bloom, M.E.; Vicentin, J.; Honeycutt, D.S. et al. Highly renewable, thermoplastic tetrapolyesters based on hydroquinone, p-hydroxybenzoic acid or its derivatives, phloretic acid, and dodecanedioic acid. *Journal of Polymer Science, Part A—Polymer Chemistry* **2018**, *56*, 1498–1507.
23. Wilsens, C.H.R.M.; Deshmukh, Y.S.; Liu, W. Processing and performance of aromatic-aliphatic thermotropic polyesters based on vanillic acid. *Polymer* **2015**, *60*, 198–206.

24. Wilsens, C.H.R.M.; Verhoeven, J.M.G.A.; Noordover, B.A.J. et al. Thermotropic Polyesters from 2,5-Furandicarboxylic Acid and Vanillic Acid: Synthesis, Thermal Properties, Melt Behavior, and Mechanical Performance. *Macromolecules*, **2014**, *47*, 3306–3316.
25. Wei, P.; Wang, L.; Huang, S. et al. Synthesis and Characterization of Novel Thermotropic Aromatic-Aliphatic Biodegradable Copolyesters Containing D,L-Lactic acid (LA), Poly(butylene terephthalate) (PBT) and Biomesogenic Units. *Polymer-Plastics Technology and Engineering* **2014**, *53*, 1697–1705.
26. Mialon, L.; Pemba, A.G.; Miller, S.A. Biorenewable polyethylene terephthalate mimics derived from lignin and acetic acid. *Green Chem.* **2010**, *12*, 1704.
27. Imasaka, K.; Nagai, T.; Yoshida, M. et al. Synthesis and in vitro degradations of low-molecular-weight copolyesters composed of L-lactic acid and aromatic hydroxy acids. *Makromol. Chem.* **1990**, *191*, 2077–2082.
28. Nicely, V.A.; Dougherty, J.T.; Renfro, L.W. Sequence Distributions and a Phase Diagram for Copolymers Made from Poly(ethy1ene terephthalate) and p-Acetoxybenzoic Acid. *Macromolecules* **1987**, *20*, 573–578.
29. Jin, X.; Carfagna, C.; Nicolais, L. et al. Synthesis and characterization of potentially biodegradable thermotropic polyesters based on p-hydroxybenzoic acid and glycolic acid. *Journal of Polymer Science Part A: Polymer Chemistry* **1994**, *32*, 3115–3122.
30. Jin, X.; Carfagna, C.; Nicolais, L. et al. Synthesis, Characterization, and in Vitro Degradation of a Novel Thermotropic Ternary Copolyester Based on p-Hydroxybenzoic Acid, Glycolic Acid, and p-Hydroxycinnamic Acid. *Macromolecules* **1995**, *28*, 4785–4794.
31. Kricheldorf, H.R.; Schwarz, G. New polymer syntheses: 10. Syntheses of high molecular weight poly(4-hydroxybenzoate)s by bulk condensations of 4-hydroxybenzoic acids. *Polymer* **1984**, *25*, 520–528.
32. Kricheldorf, H.R.; Löhden, G. Whisker 11. Poly(ester—amide)s derived from vanillic acid and 4-aminobenzoic acid. *Polymer* **1995**, *36*, 1697–1705.
33. Kricheldorf, H.R.; Stukenbrock, T. New polymer syntheses, 92. Biodegradable, thermotropic copolyesters derived from β-(4-hydroxyphenyl)propionic acid. *Macromol. Chem. Phys.* **1997**, *198*, 3753–3767.
34. Nagata, M. Synthesis, characterization, and hydrolytic degradation of copolyesters of 3-(4-hydroxyphenyl) propionic acid and p-hydroxybenzoic acid, vanilic acid, or syringic acid. *Journal of Applied Polymer Science* **2000**, *78*, 2474–2481.
35. Wilsens, C.H.R.M.; Noordover, B.A.J.; Rastogi, S. Aromatic thermotropic polyesters based on 2,5-furandicarboxylic acid and vanillic acid. *Polymer* **2014**, *55*, 2432–2439.
36. Mikhaylov, P.A.; Kalita, A.G.; Kulichikhin, V.G. Synthesis of New Thermotropic Fully Aromatic Copolyesters from Hydroxybenzoic and Hydroxybiphenylcarboxylic Acids. *Polymer Science, Series B* **2022**, *64*, 393–401.
37. Pearl, I.A. Reactions of Vanillin and Its Derived Compounds. IV.1 The Caustic Fusion of Vanillin. *J. Am. Chem. Soc.* **1946**, *68*, 2180–2181.
38. Schwarz, G.; Kricheldorf, H.R. Whiskers. 12. Whisker-like Crystals of Poly(4′-hydroxybiphenyl-4-carboxylic acid). *Macromolecules* **1995**, *28*, 3911–3917.
39. Kim, W.N.; Denn, M.M. Properties of blends of a thermotropic liquid crystalline polymer with a flexible polymer (Vectra/PET). *Journal of Rheology* **1992**, *36*, 1477–1498.
40. Huh, S.M.; Jin, J.I. Synthesis and characterization of wholly aromatic polyesters derived from 6-hydroxy-5-phenyl-2-naphthoic acid or 4′-hydroxy-3′-phenylbiphenyl-4-carboxylic acid and 4-hydroxybenzoic acid. *Macromolecules* **1997**, *30*, 3005–3013.
41. Wilsens, C.H.R.M.; Rastogi, S.; Veld, M.A.J. et al. Liquid crystalline furandicarboxylic acid-based aromatic polyesters. *Patent WO2013/092667*, **2013**.
42. Mikhailov, P.A.; Zuev, K.V.; Kulichikhin, V.G. Synthesis and Characterization of Novel Wholly Aromatic Copolyesters Based on 4′-Hydroxybiphenyl-3-Carboxylic and 3-Hydroxybenzoic Acids. *Polymers* **2023**, *15*, 2133.
43. Fernandez-Blazquez, J.P.; Bello, A.; Perez, E. Observation of Two Glass Transitions in a Thermotropic Liquid-Crystalline Polymer. *Macromolecules* **2004**, *37*, 9018–9026.
44. Shinn, T.-H.; Lin, C.-C. Co[poly(ethylene terephthalate-p-oxybenzoate)] thermotropic copolyester. II. X-ray diffraction analysis. *J. Appl. Polym. Sci.* **1993**, *47*, 1105–1113.
45. Zhang, S.; Cheng, Z.; Zeng, S. et al. Synthesis and characterization of renewable polyesters based on vanillic acid. *J. Appl. Polym. Sci.* **2020**, *137(39)*, 49189.
46. Chen, S.-C.; Zhang, X.-M.; Liu, M. et al. Rheological Characterization and Thermal Stability of Different Intrinsic Viscosity Poly(ethylene terephthalate) in Air and Nitrogen. *International Polymer Processing* **2016**, *31(3)*, 292-300.
47. Heifferon, K.V.; Spiering, G.A.; Talley, S.J. et al. Synthesis and Characterization of a Nematic Fully Aromatic Polyester Based on Biphenyl 3,4′-Dicarboxylic Acid. *Polymer Chemistry* **2019**, *10 (31)*, 4287–4296.
48. Park, G.T.; Lee, W.J.; Chang, J.-H. et al. Dependence of the Physical Properties and Molecular Dynamics of Thermotropic Liquid Crystalline Copolyesters on p-Hydroxybenzoic Acid Content. *Polymers* **2020**, *12*, 198.
49. de Kort, G.W.; Leone, N.; Stellamanns, E. et al. Effect of Shear Rate on the Orientation and Relaxation of a Vanillic Acid Based Liquid Crystalline Polymer. *Polymers* **2018**, *10*, 935.

50. de Kort, G.W.; Saidi, S.; Hermida-Merino, D. et al. Reactive Processing Route to Thermotropic Polyesters with a Low Processing Temperature and Enhanced Relaxation Time. *Macromolecules* **2021**, *54*, 1401–1413.
51. Wei, P.; Wang, Y.; Wang, Y. et al. Synthesis and Properties of Thermotropic Poly(Oxybenzoate-Co-Oxynaphthoate) Copolyester Modified by a Third AB Type Monomer. *Journal of Macromolecular Science, Part B* **2020**, *59*, 197–212.